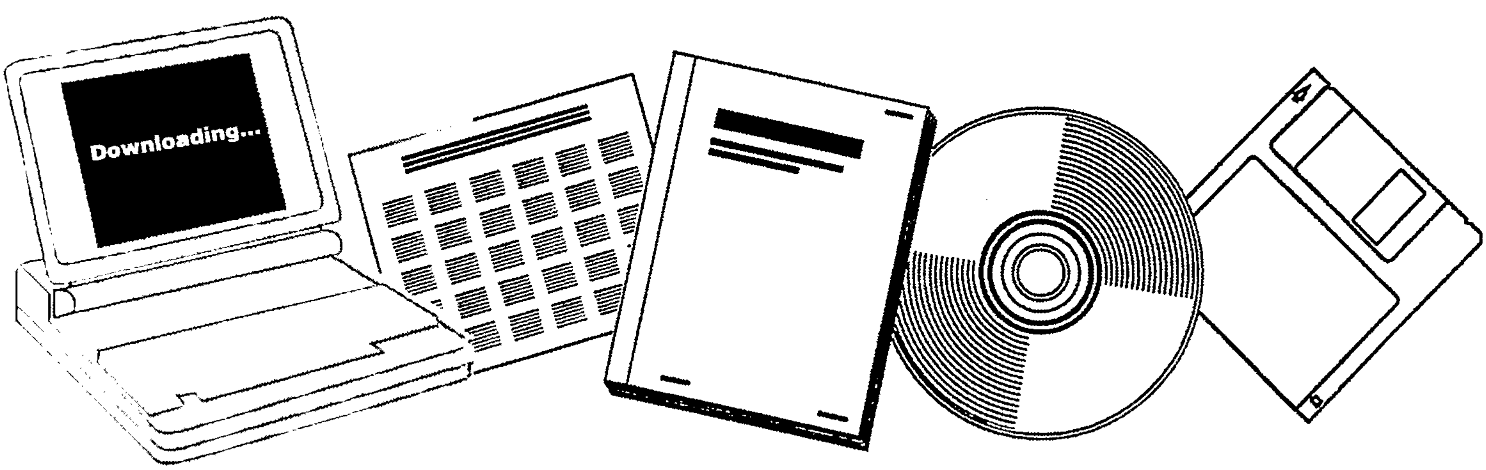
CATALYTIC COAL GASIFICATION: AN EMERGING TECHNOLOGY FOR SNG

EXXON RESEARCH AND ENGINEERING CO.,
BAYTOWN, TX. BAYTOWN RESEARCH AND
DEVELOPMENT DIV

1981



U.S. Department of Commerce
National Technical Information Service

c14,074

DOE/ET/13005--T13

DE82 007596

DE82007596

CATALYTIC COAL GASIFICATION: AN EMERGING TECHNOLOGY FOR SNG

R. R. Lessard
R. A. Reitz
Exxon Research and Engineering Company

AC01-78ET13005

It has long been known that salts of alkali metals catalyze the gasification of coal. In 1971, Exxon Research and Engineering Company discovered that potassium salts added to coal also promote the methanation of coal gasification products. This discovery led to Exxon's Catalytic Coal Gasification (CCG) process.

In the CCG process, coal with added potassium salts is gasified in a fluid bed at about 1300°F and 500 psig. Since lower temperatures and higher pressure favor methane formation, the gasification reactor has a high methane yield. By separating and recycling unconverted CO and H_2 back to the reactor, a single reaction step process is obtained.

An advantage of CCG is that the heat release from methanation is in the gasifier where it provides essentially all of the heat needed for gasification. This eliminates the need for oxygen or other complex gasifier heat input methods. Thermal efficiency of CCG ranges from 60 to 70% depending on coal feed properties.

Process development work has been carried out in bench scale equipment and pilot plants. The largest and current pilot plant is a 1 ton/day unit. This unit has a 10-inch diameter gasifier 80 ft high, gas recycle and catalyst recovery facilities. A large part of the development effort to date has been funded by the U. S. Department of Energy and the Gas Research Institute, whose support and encouragement is gratefully acknowledged.

The 1 ton/day unit has operated for over 8000 hours since its completion in 1978. Problems with agglomeration and bed density have been overcome. In April 1981, a 23-day demonstration run was completed confirming the operability of the process at the intended commercial operating conditions. This was a significant milestone in the program.

The next major phase of the CCG development program is the construction and operation of a 100 ton/day pilot plant. This unit is to be built in Holland with the objective of bringing the process to commercial readiness. The size has been carefully selected to allow direct scale-up from the 100 ton/day pilot plant to commercial sized plants.

c14,074

CATALYTIC COAL GASIFICATION
AN EMERGING TECHNOLOGY FOR SNG

Exxon Research and Engineering Co. has been engaged over the last decade in the development of a unique process for the conversion of coal to methane. Our development started with the discovery that coal catalyzed with potassium salts promotes methanation of the coal gasification products. From this discovery stemmed a one reactor process concept which offers a more efficient, lower cost route to produce methane from coal.

In this presentation, we will describe our process concept, recent development activities and plans to bring the process to commercial readiness. I'll be referring to the process by its initials - CCG - for Catalytic Coal Gasification.

The Synergism of the Potassium Catalyst

The effects of the potassium catalyst combine is a synergistic way to yield an attractive, energy efficient process concept. Let's briefly examine these effects. Potassium has been known to catalyze the carbon gasification reaction for over half a century.[1] In CCG, we take advantage of this catalytic action by gasifying coal at only 1300°F, while still obtaining reaction rates which give commercially acceptable reactor volumes. Next is the key discovery of potassium's ability to promote the methanation reaction. As shown on this slide (SLIDE 1) the equilibrium of the methanation reaction strongly favors methane as reactor temperature is lowered.

By operating the reactor at 1300°F, a high proportion of the CO and H_2 produced is converted to methane with the help of the potassium catalyst. This methanation reaction liberates a large amount of heat - fortunately in the gasifier where it is needed to offset the large amount of heat required by the endothermic gasification reaction. This can be seen in the gasifier energy balance (SLIDE 2). The net effect is about break even. We thus avoid having to add large quantities of heat by means of oxygen or heated solids addition. In actual practice, a small amount of energy must be added with the steam and recycle gas to account for the energy required to heat the coal and for heat losses. Overall, efficiency of CCG should range from about 60 to 70% depending on the feed coal properties.

This slide (SLIDE 3) summarizes the benefits of the catalyst. Besides those I've covered, two more are worth touching on. The potassium char bed is quite effective at destroying hydrocarbons heavier than methane. This is an advantage in designing gasifier overhead heat recovery equipment and environmental control facilities. Finally, the potassium helps control the swelling tendencies of bituminous coals, and thus makes CCG capable of processing a wide range of coals with minor changes in processing conditions.

Let's look at the proposed commercial plant processing sequence.[2] (SLIDE 4)

The coal is crushed and dried after which the catalyst solution is added. The moisture from the catalyst solution is evaporated, and the prepared coal is fed to the gasifier via a lock hopper system. The coal is gasified at conditions of about 1300°F and 500 psiz in a simple fluidized bed reactor containing no internals other than a gas distributor.

The gasifier effluent consists mostly of CH_4, CO_2 and unconverted steam, CO and H_2. This effluent flows through cyclones in which the coarser entrained fines are recovered for return to the reactor. After high level heat recovery from the gas, the remaining fines are removed by cyclones and a venturi scrubber, and acid gases are removed using commercially available technology. Product methane is separated from CO and H_2 by cryogenic distillation, and the methane is sent to sales. The carbon monoxide and hydrogen are recycled to the gasifier. Since the amount of CO and H_2 fed balances the amount of CO and H_2 leaving the gasifier, the net products of gasification are only methane and CO_2, along with small amounts of H_2S and NH_3.

Also shown on the flow diagram is a catalyst recovery step. This is required because catalyst leaves the gasifier with the ash/char residue, and the catalyst is too costly to discard. Fortunately, most of the catalyst is water soluble. However, a portion of the catalyst reacts with the coal ash to form insoluble compounds, principally potassium aluminum silicates. The degree of catalyst tie-up is a function of the coal ash level and composition. With Illinois coal and a typical initial loading of 15 wt% catalyst (as K_2CO_3 equivalent), about 70% of the catalyst is water soluble. Thus, some makeup catalyst in the form of KOH or K_2CO_3 is required.

The use of potassium as a catalyst in our process also brings some debits (SLIDE 5). One debit is the facilities I just mentioned which are required to recover catalyst, and the need for fresh makeup catalyst. Another is the higher quality construction materials required to offset the corrosive effects of the potassium salts present. This problem is somewhat mitigated by the lower 1300°F operating temperature of the process. Another debit is the greater volume of residual ash to be disposed, consisting of the coal ash, some unconverted carbon since carbon conversion is limited by the fluid bed concept used, and unrecovered insoluble salts of potassium. We believe that the unconverted carbon and insoluble potassium will not cause any additional environmental disposal problems, and are working to qualify our residue for various disposal and utilization options.

Development Activities

Advancement of CCG technology through its various development stages, has involved an integrated program combining fundamental bench research, pilot plant testing, and engineering guidance. This slide (SLIDE 6) presents a cross-section of the various test units used to collect experimental data over the last decade, as well as a look ahead to the future large pilot plant and commercial gasifiers.

Initially, bench scale equipment using less than 20 grams of coal per test produced critical data on reaction kinetics, catalyst activity, and efficiency of potassium recovery. Subsequently, 50-200 lb/day continuous pilot plant systems were designed and constructed as the process continued to evolve toward commercialization. Along this development path, critical funding was provided by the U.S. Department of Energy and the Gas Research Institute and we owe both a debt of gratitude. Currently the project is being totally funded by Exxon.

The program is now in the process development phase and the experimental workhorse being used is our 1 Ton/Day (TPD) Process Development Unit (PDU) located at our synthetic fuels laboratory in Baytown, Texas. This unit is large enough to permit continuous feed and withdrawal, and it operates at the projected commercial operating conditions. The PDU includes complete facilities for coal preparation, gasification, product gas cleanup/separation and catalyst recovery. The gasifier is a slender tube 10 inches in diameter and 80 feet long. Here is a picture (SLIDE 7) of the PDU under construction back in 1978. The reactor and feed equipment are contained in a 12-story tower while product gas separation and catalyst recovery equipment are in adjacent facilities.

This next slide (SLIDE 8) is a detailed schematic of the tower structure which contains the gasification section. The PDU is completely automated and data acquisition is accomplished by computer. About 1000 process variables are continuously monitored and reported as hourly averages.

The purpose of the 1 TPD unit has been to confirm the operability of the process at commercial operating conditions and to provide the data base for design of the large pilot plant (the next phase of this program). To date, the unit has been run for over 8,000 hours, with the longest uninterrupted run period being 33 days. We are proud of our operating achievements, especially in view of the substantial challenge which operation of high pressure coal pilot plants presents.

Following startup of PDU, several major problems were encountered. In each case our integrated program (research/pilot plant/engineering) addressed and resolved these problems while continuing to confirm CCG as an economically attractive coal-to-methane process. In early operations coal agglomerates caused plugging problems in the feed and withdrawal lines. Analyses indicated that these agglomerates were ash particles "cemented" together by water soluble potassium carbonate. Process variable studies showed that these agglomerates formed near the point where coal enters the fluid bed. The problem was solved by increasing the velocity of injected coal, thereby minimizing the probability of the fresh coal particles sticking together before being dispersed in the fluidized bed.

A second major problem encountered and resolved was the finding that the gasifier fluid bed density was only one-third of what had been predicted based on the predevelopment work (5 vs 15 lb/ft^3). It became clear that Illinois No. 6 coal becomes plastic and swells when brought rapidly to temperature in the gasifier. It then puffs like popcorn due to evolution of gases and breaks down into fine particles as a result of attrition in the fluid bed. A preoxidation step was identified as the preferred near-term solution to this problem. Since being implemented, this solution has been significantly improved and has been so effective that densities up to twice the original target were achieved during 1981.

After overcoming these and a few other obstacles, the PDU achieved its most significant milestone to date in April, 1981, with a 23-day demonstration run. This run showed the operability, sustainability and control of the CCG process at the target commercial conditions. The results of this run are shown on the next slide (SLIDE 9). During this 23-day period, operations were generally stable and a total of fourteen material balance periods were obtained, with each representing a 24-hour period of stable performance.

Coal and steam rates were maintained near the target and temperature and pressure were controlled at 1280°F and 500 psia, respectively. The fluid bed density was held at 15 pounds/ft^3, steam conversion was 35% and carbon conversion was 85-90%--all met the original targets. Methane content in the product gas was 20-25%, somewhat lower than target, but this level was consistent with the high steam/coal ratio used. Material balances within 5% were recorded and no gasifier plugging was observed. This run was a major success. It demonstrated process operability and provided data necessary for the design of the large pilot plant. The PDU is now focusing on evaluation of alternate coals, process improvements and improved carbon conversion.

Large Pilot Plant Chosen to Achieve Commercial Readiness

A challenge faced by all process developers is what size demonstration unit is required to have an acceptable risk level for a first commercial size plant. Developers of coal to synfuels processes must take into account that a commercial plant is likely to be large and very expensive, and that coal conversion technology has several frontier areas. The resources and philosophy of the process developer and first user are also important factors.

We have given this question serious study for the CCG process, and have concluded a large pilot plant of about 100 TPD capacity is needed to bring the process to commercial readiness. I would like to cover the key reasoning behind our decision.

Four factors must be taken into account in large pilot plant size selection: process issues, hardware issues, scaleup capability, and commercial representativity. Our examination of the CCG process against these factors led us to select the size based upon the gasifier. This is as expected, since the other process steps such as acid gas removal, cryogenics, catalyst recovery equipment, etc., are based on available technology.

This slide (SLIDE 10) shows the results of the study, based upon commercial reactors capable of handling 3000 to 4000 TPD of coal.

Fluid bed considerations help establish reactor diameter. We have a gasifier kinetic model based on chemical engineering principles and our 1 TPD unit experience. To design a commercial reactor, this kinetic model must be validated in a unit where wall effects are not controlling and flow patterns are similar to those expected in a commercial reactor. A critical region in our gasifier is the feed coal mixing zone, for it is in this zone at the bottom of the reactor where feed coal, steam and recycle gas enter, and where converted char is withdrawn. It is important that this zone be commercially representative.

Heat loss effects are very important from the standpoint of process issues. As the demonstration unit size gets smaller, heat losses go up disproportionately. This results in higher CO and H_2 recycle gas rates and higher preheat temperatures being required to heat balance the unit. This in turn affects the kinetic rates of gasification and methanation and the critical feed coal mixing zone. Since this problem can only be overcome in larger size units, some compromise is necessary. We have elected to be within 25% of expected commercial kinetic rates for the pilot plant. This was a governing area in the size selection.

Reactor velocity should be at commercial levels for fluid bed processes to establish bed particle size distribution and overhead solids entrainment.

Our reactor design concept calls for cold walls - that is, less than 600°F design temperature - with refractory lining. The gas distribution grid design is also specific to the process. It will operate at high temperatures because of the 1300°F reactor bed temperature and the need to preheat steam and recycle gas to temperatures higher than 1300°F. Materials of construction are important in both these areas. The large pilot plant gasifier will use the same design concepts as a commercial unit.

Another important area is the coal feed system, from pressurization through the injection nozzles. Important considerations in the LPP nozzle design are the nozzle geometry, the coal capacity per nozzle and injection gas rate. All must be representative of expected commercial design parameters. An added constraint for the pilot plant is the minimum diameter nozzle to handle the anticipated 8 mesh coal top size. This area is also one which governed the unit size selection.

Another area of the process requiring demonstration is the overhead heat transfer. First, gasifier effluent is used to heat recycle gas and then to generate steam. The first gas-to-gas heat exchanger is important for process efficiency. Fouling must not be severe. The exchanger must stand up mechanically to a high temperature, high pressure, dusty environment. Materials of construction must be proven.

Large Pilot Plant Design Challenges

After establishing the size of the large pilot plant, the design stage offers new challenges. Once again, we strive for scale up capability, commercial representativity where warranted, plus the ability to gather the needed data. Some examples are listed on this slide.[3] (SLIDE 11). The solids entrainment rate in the gasifier is an area of uncertainty. If the gas scrubbing system is designed for a maximum expected load, it may have so much over-capacity that normal rates will not give meaningful performance data. In catalyst recovery, our goal is to obtain data to design commercial solid/liquid separation devices. But uncertainties in filter cake resistance and operability considerations push for over-capacity in the large pilot plant. A similar challenge exists for holdup in the catalyst recovery loop. Surge capacity is desirable from an operability standpoint. Yet, we want to minimize inventory holdup time from a process standpoint. Thus, the design of large pilot plants must be carefully thought out and considered from many different needs.

Planning Basis for the Large Pilot Plant

The planning basis for the 100 TPD pilot plant is shown on this slide (SLIDE 12). We are currently in the process design phase. Letting of the prime contract is planned for 1983, which will lead to detailed engineering, procurement and construction in the 1983 to 1985 time period. Operation will be in 1986 through 1988, with a possible additional year to demonstrate process improvements currently in early stages of development.

The pilot plant will be built in Rotterdam Europort in Holland by Esso Steenkool Technologie, an Exxon affiliate. A site next to an existing Exxon facility has been selected to take advantage of certain available utilities. Holland has been selected because Northern Europe, and Holland in particular, are likely locations for SNG from coal plants to augment existing and expanding gas networks.

The 100 TPD pilot plant activity and its associated R&D are expected to cost over 500 M$. This is certainly a large R&D expenditure and represents a significant undertaking. Two important factors are reflected in the decision to embark on this effort. First, is an outlook which says that SNG from coal is an economically viable commercial concept. Second, is that the large pilot plant is a reasonable development route. We have concluded that a large pilot plant will allow us to design a commercial plant without going to an intermediate size demonstration unit. In addition, the large pilot plant is expected to yield an improved design basis and improved service factor for the first commercial plant. Overall, we believe the benefits from the large pilot plant will more than overcome its cost when CCG is practiced commercially.

Concluding Remarks

Exxon believes that CCG offers a more efficient, lower cost route to SNG from coal. Several years of development work have brought the process from its early concepts to a point where its process feasibility has been demonstrated. The DOE and GRI played an important part in CCG's evolution through their financial support and encouragement. Exxon is now embarking on the final development step - the design of a large pilot plant - to ready CCG for commercial application.

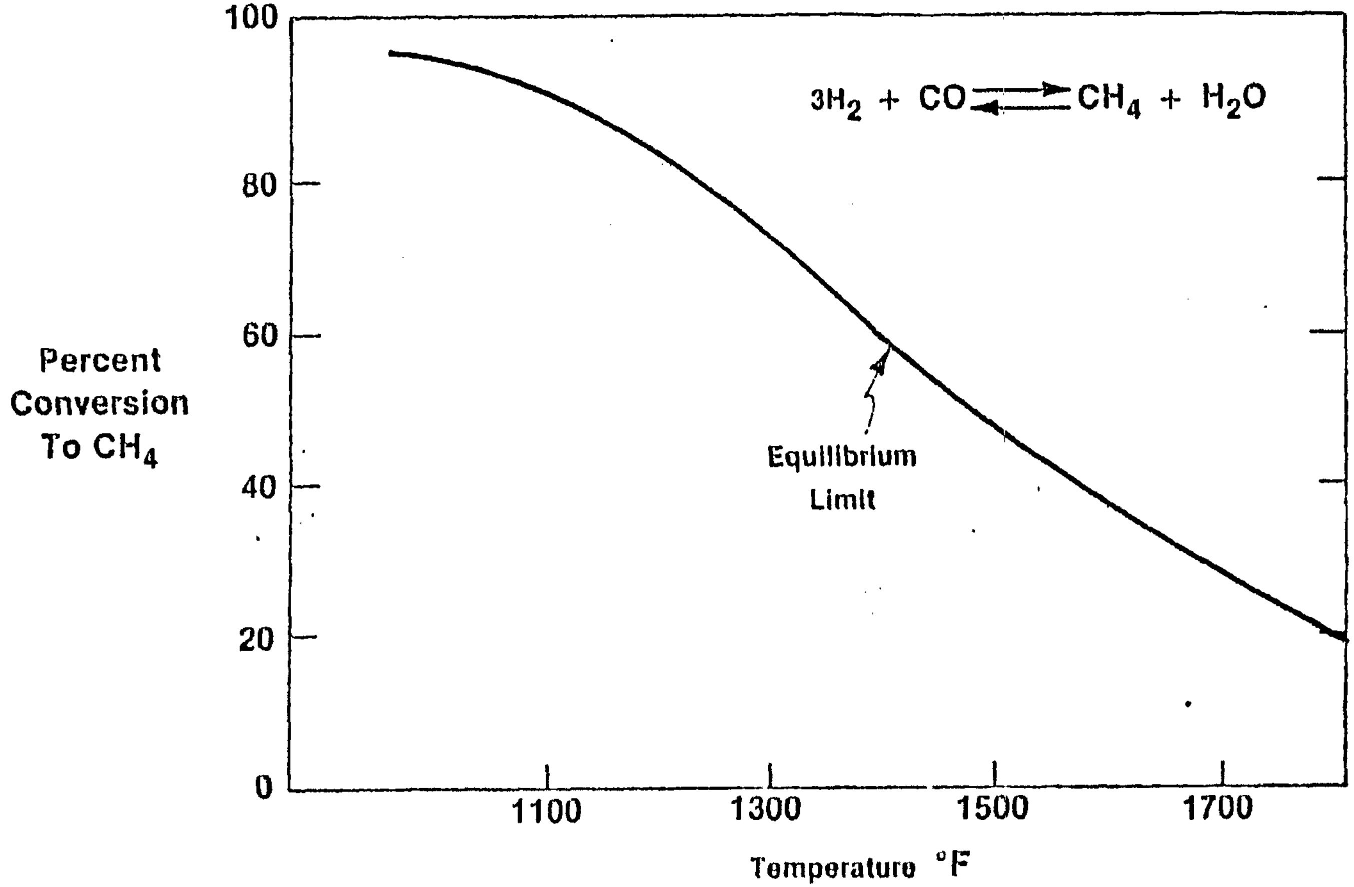
REFERENCES CITED

(1) Taylor, H. S. and H. A. Neville, "Catalysis in the Interaction of Carbon and Steam Dioxide," J. Am. Chem. Soc., 43:2065-71 (1921).

(2) Hirsch, R. L. , J. E. Gallagher, Jr. and C. A. Eucker, "Exxon's Catalytic Coal Gasification Process," presented at the 1981 International Gas Research Conference, Los Angeles, CA, September, 1981.

(3) Nahas, N. C., "Catalytic Coal Gasification," presented at the Exxon Engineering Symposium, Florham Park, NJ, December, 1981.

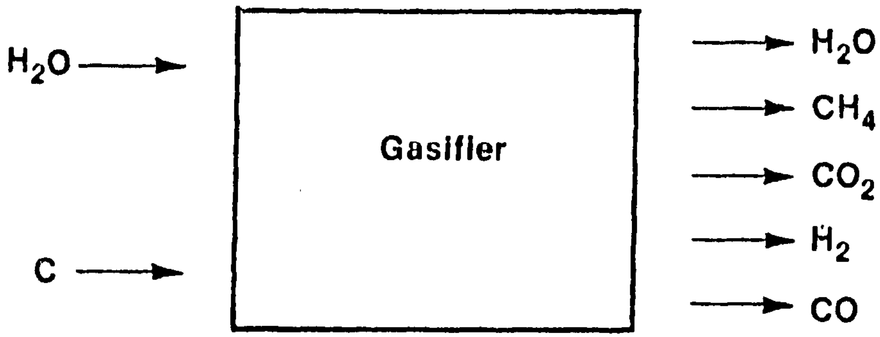
METHANATION FAVORED AT LOW TEMPERATURES



182031

-15-

COAL GASIFICATION CHEMISTRY



$2C + 2H_2O \longrightarrow 2H_2 + 2\,CO$	Δ Hr = 64 kcal Gasification
$CO + H_2O \longrightarrow CO_2 + H_2$	Δ Hr = .8 kcal Shift
$3H_2 + CO \longrightarrow CH_4 + H_2O$	Δ Hr = .54 kcal Methanation

---

$2H_2O + 2C \longrightarrow CH_2 + CO_2$	Δ Hr = 2 kcal Overall

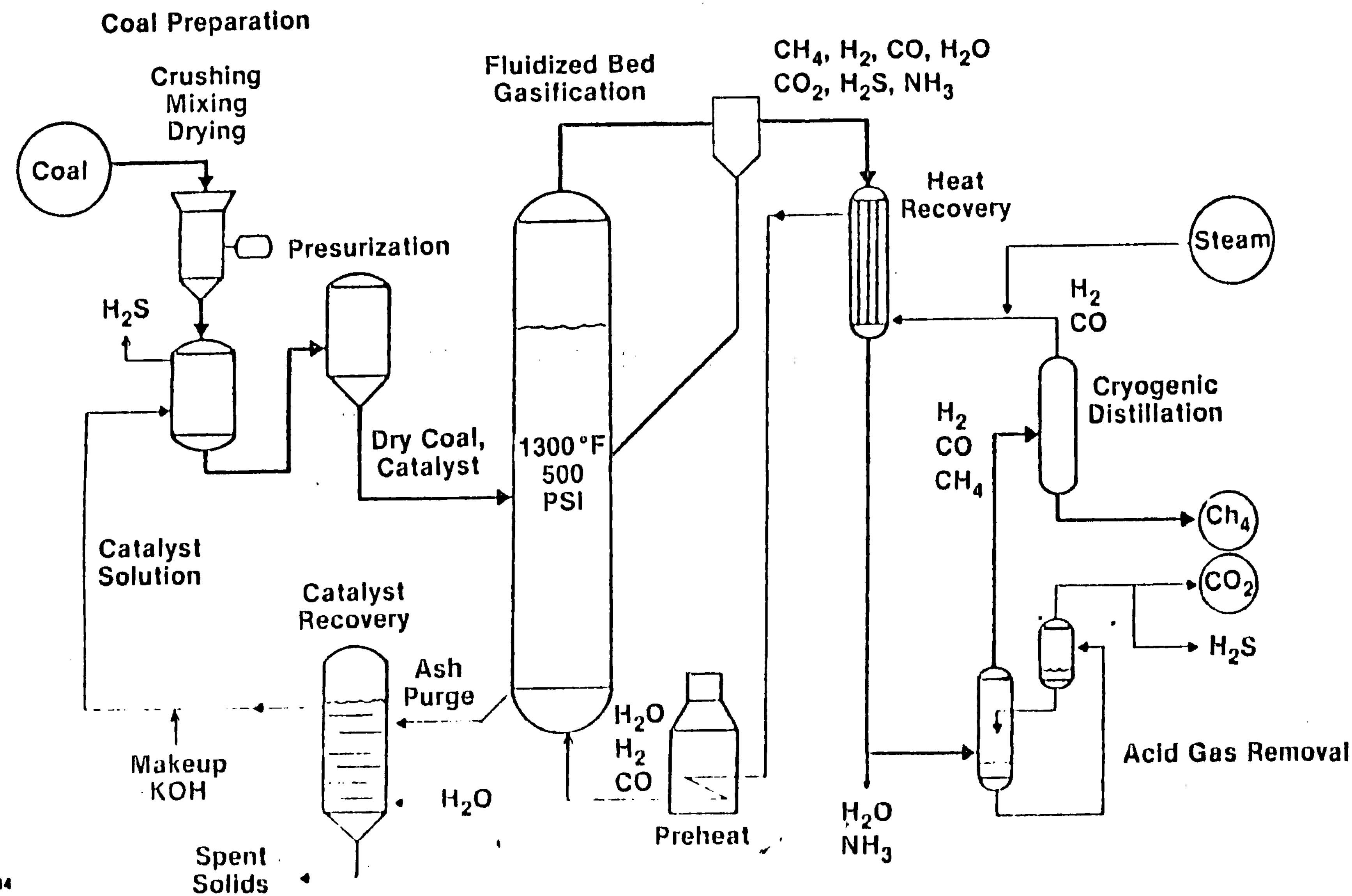
102032

SYNERGISM OF POTASSIUM CATALYST

- Accelerates Gasification Kinetic Rate
  — Commercially Acceptable Reactor Volume at 1300 °F
- Promotes Methanation Kinetic Rate
  — Equilibrium More Favorable at 1300 °F
- Gasifier Almost Thermally Neutral
  — $2C + 2H_2O \rightleftharpoons CH_4 + CO_2$ 2 K Cal
- Tars/Heavy Oil Normally Destroyed in Reactor
- Reduces Coal Swelling Upon Devolatilization

102033

SNG FROM CATALYTIC COAL GASIFICATION



182034

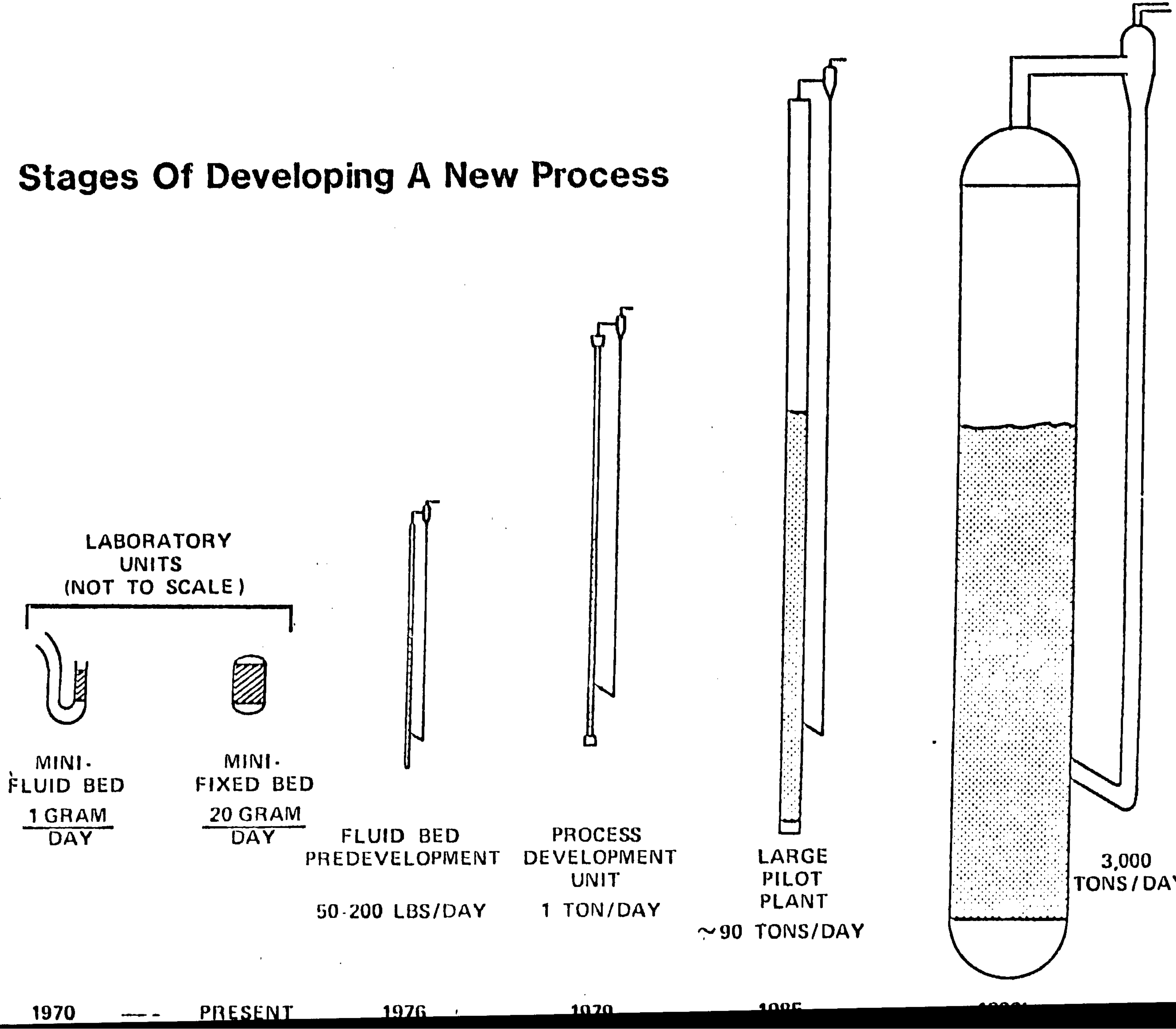
CATALYTIC GASIFICATION

- Synergism of Potassium Catalyst
  - Accelerates Gasification Kinetic Rate
  - Promotes Methanation Kinetic Rate
  - Gasifier Almost Thermally Neutral
  - Tars/Heavy Oils Normally Destroyed in Reactor
  - Reduces Coal Swelling Upon Devolatilization

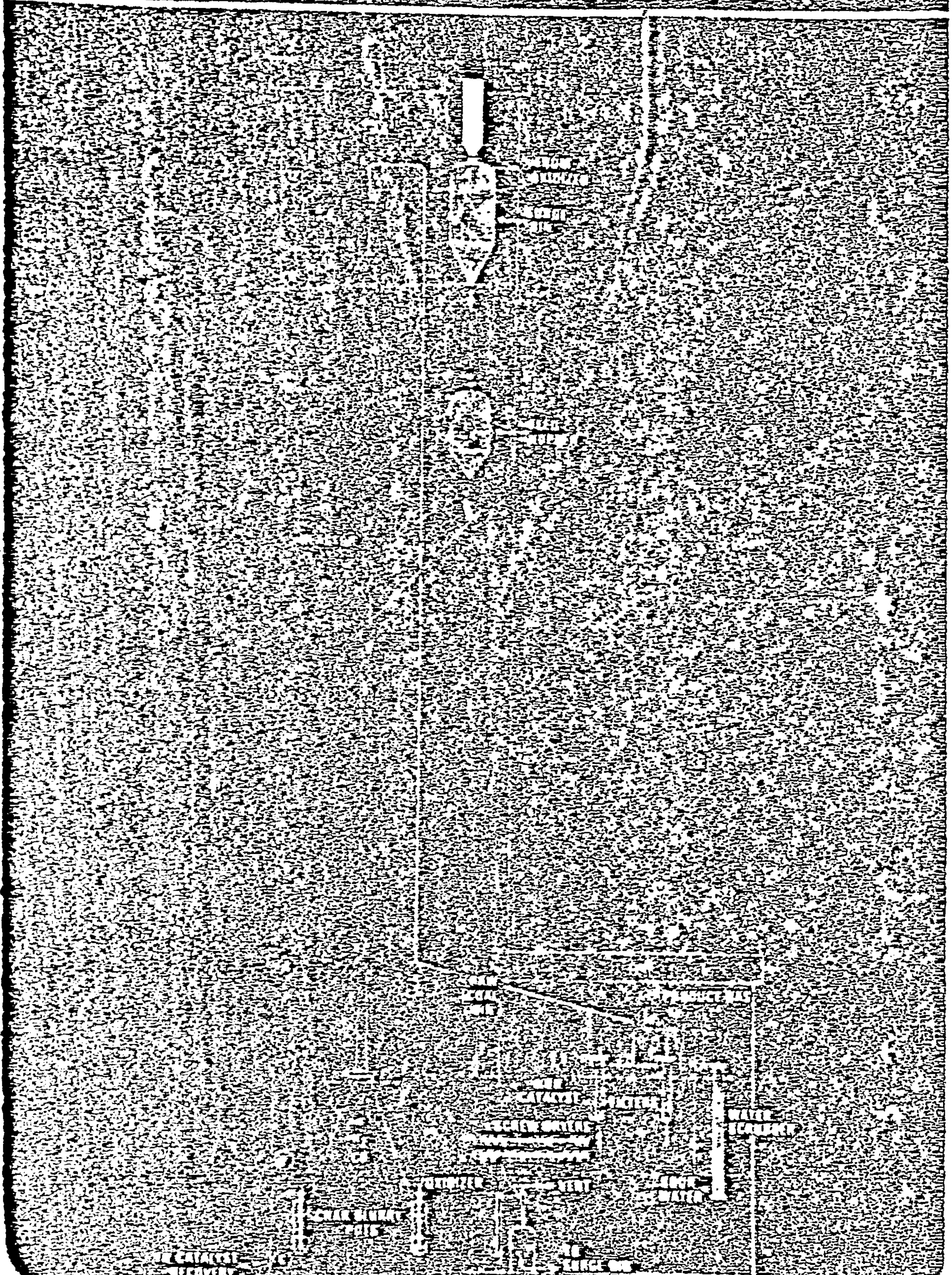
- Process Debits
  - Catalyst Recovery and Makeup
  - Corrosiveness of Potassium Salts
  - Residual Solids Contain Coal Ash, Unconverted Carbon and Insoluble Potassium Salts

182035

Stages Of Developing A New Process



PDU TOWER CROSS-SECTION



SUCCESSFUL 23 DAY PDU GASIFIER DEMONSTRATION RUN WAS ACHIEVED

	TARGETS	ACHIEVED
TEMPERATURE	1300°F	1280°F
PRESSURE	500 PSIA	500 PSIA
COAL + CATALYST	132 LBS/H	132 LBS/H
STEAM/COAL RATIO	1.7	1.9
BED DENSITY	>10 LBS/FT^3	16 LBS/FT^3
SYN GAS BALANCE	>80%	71-92%
STEAM CONVERSION	30-40%	35%
CARBON CONVERSION	>85%	85-90%
CH_4 IN PRODUCT GAS	>25%	21%*
RUN LENGTH	14-21 DAYS	23 DAYS

* Consistent With Operating Conditions

LARGE PILOT PLANT SIZE STUDY

	Scale Up Considerations
Reactor	— Minimize Wall Effects in Fluid Bed
	— Feed Coal Mixing Zone
	— Heat Loss Effects
	— Velocity
	— Reactor Design
	— Feed Coal Injection System
Overhead Heat Recovery	— Fouling
	— Mechanical Design

182036

EXAMPLES OF PILOT PLANT DESIGN CHALLENGES

- Split between entrained solids and ash purge from the bed — particulate scrubbing capacity for maximum loading?
- Solid-liquid separation in catalyst recovery — system for highest expected filter cake resistance?
- Catalyst holdup in the recovery loop — surge capacity?
- In general — design systems with wide ranges in capacity that generate good data at low loadings.

[illegible]

LARGE PILOT PLANT CONSTRUCTION AND OPERATION — PLANNING BASIS

Size:	100 T/D Coal Feed	
Location:	Rotterdam Europoort	
Timing:	Design	1982
	Construction	1983-85
	Operation	1986-88
Program Cost:	500 M$ +	

100004

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000